

# Hallmarks of Hund's coupling in the Mott insulator $\text{Ca}_2\text{RuO}_4$

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A paradigmatic case of multi-band Mott physics including spin-orbit and Hund's coupling is realised in  $\text{Ca}_2\text{RuO}_4$ . Progress in understanding the nature of this Mott insulating phase has been impeded by the lack of knowledge about the low-energy electronic structure. Here we provide – using angle-resolved photoemission electron spectroscopy – the band structure of the paramagnetic insulating phase of  $\text{Ca}_2\text{RuO}_4$  and show how it features several distinct energy scales. Comparison to a simple analysis of atomic multiplets provides a quantitative estimate of the Hund's coupling  $J = 0.4$  eV. Furthermore, the experimental spectra are in good agreement with electronic structure calculations performed with Dynamical Mean-Field Theory. The crystal field stabilisation of the  $d_{xy}$  orbital due to  $c$ -axis contraction is shown to be important in explaining the nature of the insulating state. It is thus a combination of multiband physics, Coulomb interaction and Hund's coupling that generates the Mott insulating state of  $\text{Ca}_2\text{RuO}_4$ . These results underscore the importance of Hund's coupling in the ruthenates and related multiband materials.

Electronic instabilities driving superconductivity, density wave orders and Mott metal-insulator transitions produce a characteristic energy scale below an onset temperature<sup>1–3</sup>. Typically, this energy scale manifests itself as a gap in the electronic band structure around the Fermi level. Correlated electron systems have a tendency for avalanches, where one instability triggers or facilitates another<sup>4</sup>. The challenge is then to disentangle the driving and secondary phenomena. In many Mott insulating systems, such as  $\text{La}_2\text{CuO}_4$  and  $\text{Ca}_2\text{RuO}_4$ , long-range magnetic order appears as a secondary effect. In such cases, the energy scale associated with the Mott transition is much larger than that of magnetism. The Mott physics of the half-filled single band  $3d$  electron system  $\text{La}_2\text{CuO}_4$  emerges due to a high ratio of Coulomb interaction to band width. This simple scenario does not apply to  $\text{Ca}_2\text{RuO}_4$ . There, the orbital and spin degrees of freedom of the  $2/3$ -filled (with four electrons)  $t_{2g}$ -manifold implies that Hund's coupling enters as an important energy scale<sup>5</sup>. Moreover, recent studies of the antiferromagnetic ground state of  $\text{Ca}_2\text{RuO}_4$  suggest that spin-orbit interaction also plays a significant role in shaping the magnetic moments,<sup>6–8</sup> as well as the splitting of the

$t_{2g}$  states<sup>9</sup>.

Compared to  $\text{Sr}_2\text{RuO}_4$ <sup>10,11</sup>, which may realize a chiral  $p$ -wave superconducting state, relatively little is known about the electronic band structure of  $\text{Ca}_2\text{RuO}_4$ <sup>12</sup>. Angle integrated photoemission spectroscopy has revealed the existence of Ru-states with binding-energy 1.6 eV<sup>13</sup> – an energy scale much larger than the Mott gap  $\sim 0.4$  eV estimated from transport experiments<sup>14</sup>. Moreover, angle resolved photoemission spectroscopy (ARPES) experiments on  $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{RuO}_4$  – the critical composition for the metal-insulator transition – have lead to contradicting interpretations<sup>15,16</sup> favouring or disfavouring the so-called orbital selective scenario where a Mott gap opens only on a subset of bands<sup>17,18</sup>. Extending this scenario to  $\text{Ca}_2\text{RuO}_4$  would imply orbital dependent Mott gaps<sup>18</sup>. The electronic structure should thus display two Mott energy scales (one of  $d_{xy}$  and another for the  $d_{xz}, d_{yz}$ -states). A different explanation for the Mott state of  $\text{Ca}_2\text{RuO}_4$  is that the  $c$ -axis compression of the S-Pbca insulating phase induces a crystal field stabilisation of the  $d_{xy}$  orbital, leading to half-filled  $d_{xz}, d_{yz}$  bands and completely filled  $d_{xy}$  states<sup>19,20</sup>. In this case only one Mott gap on the  $d_{xz}, d_{yz}$  bands will be present with band

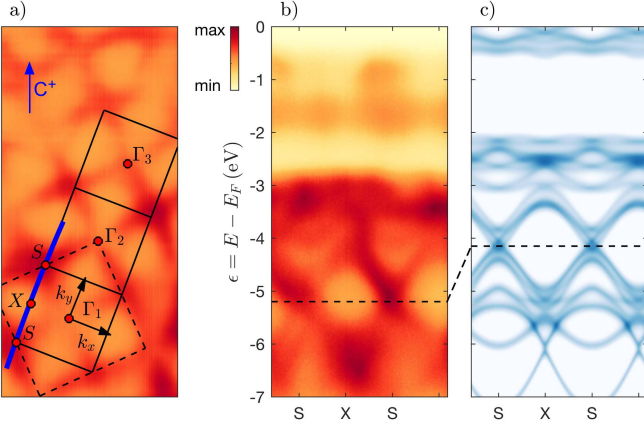


FIG. 1: **Oxygen band structure of  $\text{Ca}_2\text{RuO}_4$ .** Angle resolved photoemission spectroscopy spectra recorded with right-handed circularly polarised ( $C^+$ ) 65 eV photons in the paramagnetic (150 K) insulating state of  $\text{Ca}_2\text{RuO}_4$ , compared to DFT band structure calculations. Incident direction of the light is indicated by the blue arrow. (a) Constant energy map displaying the photoemission spectral weight at  $\epsilon = E - E_F = -5.2$  eV. Solid and dashed lines mark the in-plane projected orthorhombic and tetragonal zone boundaries, respectively.  $\Gamma_i$  with  $i = 1, 2, 3$  label orthorhombic zone centres. S and X label the zone corners and boundaries respectively. (b) Spectra recorded along the zone boundary [blue line in (a)]. Oxygen dominated bands are found between  $\epsilon = -7$  eV and  $-3$  eV whereas the ruthenium bands are located above  $-2.5$  eV. (c) First principle Density Functional Theory band structure calculation. Within an arbitrary shift, indicated by the dashed line, qualitative agreement with the experiment is found for the oxygen bands.

insulating  $d_{xy}$  states. The problem has defied a solution due to a lack of experimental knowledge about the low-energy electronic structure.

Here we present an ARPES study of the electronic structure in the paramagnetic insulating state (at 150 K) of  $\text{Ca}_2\text{RuO}_4$ . Three different bands – labeled  $\mathcal{A}$ ,  $\mathcal{B}$  and  $\mathcal{C}$  band – are identified and their orbital character is discussed through comparison to first principle Density Functional Theory (DFT) band structure calculations. The observed band structure is incompatible with a single insulating energy scale acting uniformly on all orbitals. A phenomenological Green’s function incorporating an enhanced crystal field and a spectral gap in the self-energy is used to describe the observed band structure on a qualitative level. Further insight is gained from Dynamical Mean-Field Theory (DMFT) calculations including Hund’s coupling and Coulomb interaction. The Hund’s coupling splits the  $d_{xy}$  band allowing quantitative estimate of this parameter. The Coulomb interaction is mainly responsible for the insulating behaviour of the  $d_{xz}$ ,  $d_{yz}$  bands. These experimental results, together with our theoretical analysis, elucidate the nature of the Mott phase of the prototypical multi-orbital Mott system  $\text{Ca}_2\text{RuO}_4$ . Furthermore, they

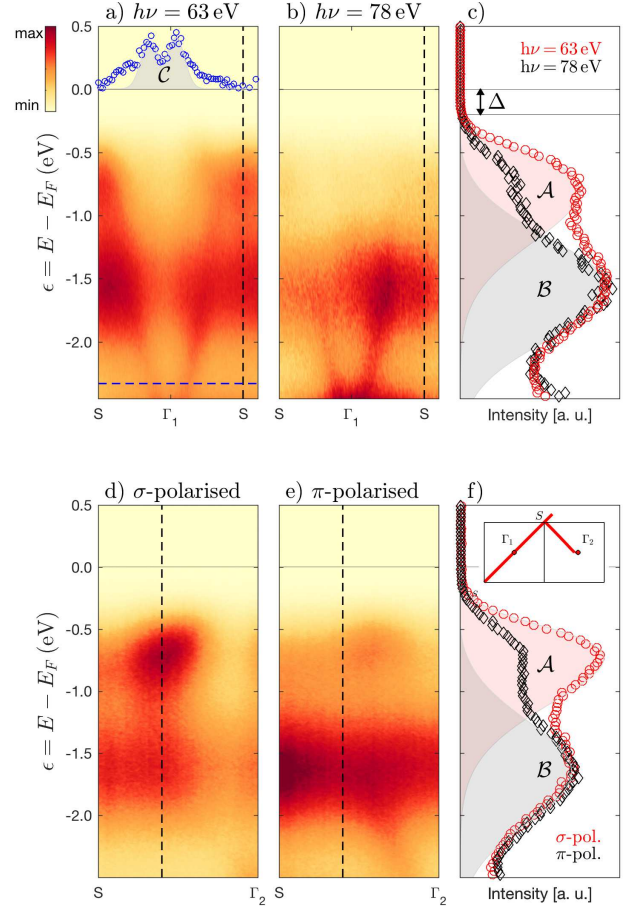


FIG. 2: **Ruthenium band structure.** (a)–(b) Photoemission spectra recorded along the high-symmetry direction  $\Gamma_1$ -S for incident circularly polarised light with photon energies  $h\nu$  as indicated. Blue points in (a) show the momentum distribution curve at the binding energy indicated by the horizontal dashed line. The double peak structure is attributed to the  $\mathcal{C}$ -band. (c) Energy distribution curves (EDCs) at the S-point, normalized at  $\epsilon = E - E_F = -1.8$  eV. (d)–(e) Linear light polarisation dependence along the S- $\Gamma_2$  direction at  $h\nu = 65$  eV. (f) EDCs at the momentum indicated by the vertical dashed lines. In both (c) and (f), the  $\mathcal{A}$ - and  $\mathcal{B}$ -bands are indicated by red and grey shading.

provide a natural explanation as to why previous experiments have identified different values for the energy gap.

## Results

**Crystal and electronic structure:**  $\text{Ca}_2\text{RuO}_4$  is a layered perovskite, where the Mott transition coincides with a structural transition at  $T_s \sim 350$  K, below which the  $c$ -axis lattice constant is reduced. We study the paramagnetic insulating state ( $T = 150$  K) of  $\text{Ca}_2\text{RuO}_4$  with orthorhombic S-Pbca crystal structure ( $a = 5.39$  Å,  $b = 5.59$  Å and  $c = 11.77$  Å). It is worth noting that due to this nonsymmorphic crystal structure,  $\text{Ca}_2\text{RuO}_4$  could not form a Mott insulating ground state at other

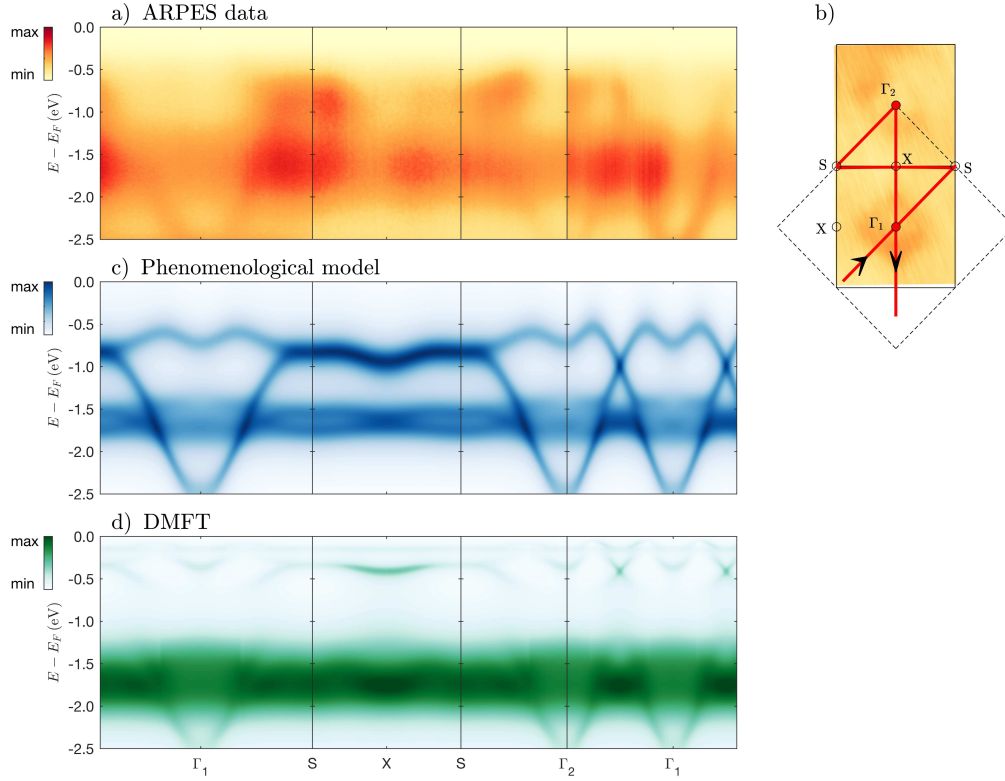


FIG. 3: **Band structure along high-symmetry directions** (a) ARPES spectra recorded along high symmetry directions with 65 eV circularly polarised light. (b) Constant energy map at  $E - E_F = -2.7$  eV. (c) DFT-derived spectra for  $\text{Ca}_2\text{RuO}_4$ , upon inclusion of a Mott gap  $\Delta_{xz/yz} = 1.55$  eV acting on  $d_{xz}$ ,  $d_{yz}$  bands and an enhanced crystal field  $\Delta_{\text{CF}} = 0.6$  eV, shifting spectral weight of the  $d_{xy}$  bands (for details, see method section) and plotted with spectral weight representation. (d) DMFT calculation of the spectral function, with Coulomb interaction  $U = 2.3$  eV and a Hund's coupling  $J = 0.4$  eV.

fillings than  $1/3$  and  $2/3$ <sup>21</sup>. In Fig. 1, the experimentally measured electronic structure is compared to a first-principle DFT calculation of the bare non-interacting bands. We observe two sets of states: near the Fermi level the electronic structure is comprised of Ru-dominated bands, while oxygen bands are present only for  $\epsilon = E - E_F < -2.5$  eV. Up to an overall energy shift, good agreement between the calculated DFT and observed  $\text{Ca}_2\text{RuO}_4$  oxygen band structure is found.

**Non-dispersing ruthenium bands:** The structure of the ruthenium bands near the Fermi level is the main topic of this paper, as these are the states influenced by Mott physics. A compilation of ARPES spectra, recorded along high-symmetry directions, is presented in Figs. 2 and 3a. In consistency with previous angle-integrated photoemission experiments<sup>13</sup>, a broad and flat band is found around the binding energy  $\epsilon = -1.7$  eV. However, we also observed spectral weight closer to the Fermi level ( $\epsilon \sim -0.8 \pm 0.2$  eV), especially near the zone boundaries (see Fig. 2a,d). These two flat ruthenium bands (labeled  $\mathcal{A}$  and  $\mathcal{B}$ ) are revealed as a double peak structure in the energy distribution

curves (EDCs) – Fig. 2c,f. Between the  $\mathcal{A}$ -band and the Fermi level, the spectral weight is suppressed. In fact, complete suppression of spectral weight is found for  $-0.2 \text{ eV} < \epsilon < 0 \text{ eV}$  (see Fig. 2c). The Mott gap, defining the energy scale between lower and upper Hubbard bands, has previously been associated with an activation energy scale  $\sim 0.4$  eV derived from resistivity measurements<sup>14</sup>. Assuming that the Fermi level is centred approximately symmetrically between lower and upper Hubbard bands, our spectroscopic observation is consistent with the transport experiments.

**Fast dispersing ruthenium bands:** In addition to the flat  $\mathcal{A}$  and  $\mathcal{B}$  bands, a fast dispersing circular shaped band is observed (Fig. 3b) around the  $\Gamma$ -point (zone centre) in the interval  $-2.5 \text{ eV} < \epsilon < -2 \text{ eV}$  – see Figs. 2a,b and 3a. A weaker replica of this band is furthermore found around  $\Gamma_2$  (Fig. 3a,b). The band velocity, estimated from momentum distribution curves (MDC's) (Fig. 2a), yields  $v = (2.6 \pm 0.4) \text{ eV \AA}$ . As this band, which we label  $\mathcal{C}$ , disperses away from the zone centre, it merges with the most intense flat  $\mathcal{B}$ -band. From the data, it is difficult to conclude with certainty

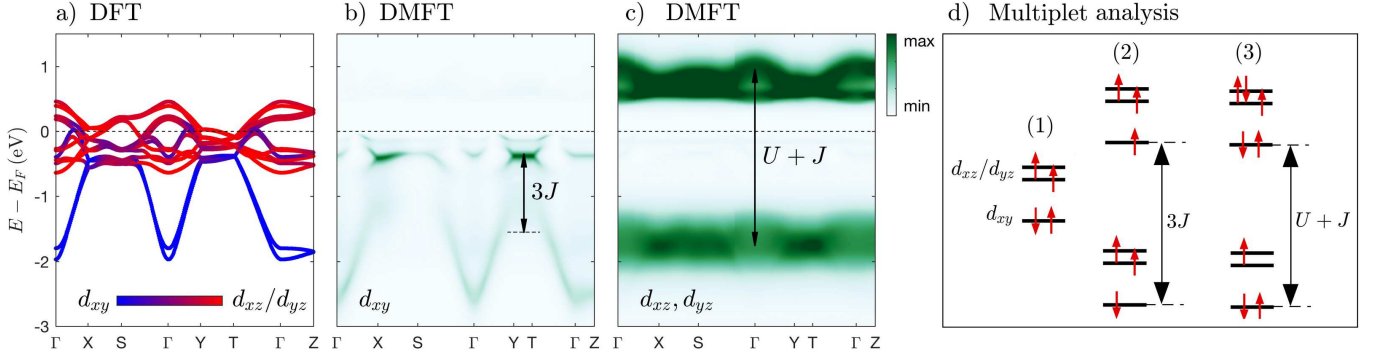


FIG. 4: **Calculated orbital band character.** (a) DFT calculation of the bare band structure.  $d_{xy}$ - and  $d_{xz}, d_{yz}$ -characters are indicated by blue and red colors respectively. (b) and (c) are the spectral function calculated within the DMFT approach and projected on the  $d_{xy}$  and  $d_{xz}, d_{yz}$  orbitals respectively. The indicated energy splittings stem from a  $t_{2g}$  multiplet analysis in the atomic limit (d): (1) Ground state multiplet defined by the crystal field and Hund's coupling  $J$ . (2)  $d_{xy}$  electron removal configurations, split by  $3J$  (see main text for explanation). (3) Representation of the twofold degenerate  $d_{xz}, d_{yz}$  electron addition and removal states, split by  $U + J$ .

whether the  $\mathcal{C}$ -band disperses between the  $\mathcal{A}$  and  $\mathcal{B}$  bands. As this feature is weak in the spectra recorded with 78 eV photons (Fig. 2b), it makes sense to label  $\mathcal{A}$  and  $\mathcal{C}$  as distinct bands.

**Orbital band character:** Next we discuss the orbital character of the observed bands. As a first step, comparison to the band structure calculations is made. Although details can vary depending on exact methodology, all band structure calculations of  $\text{Ca}_2\text{RuO}_4$  find a single fast dispersing branch<sup>22–25</sup>. Our DFT calculation reveals that the fast dispersing band has predominantly  $d_{xy}$  character (Fig. 4a). We thus conclude that the in-plane extended  $d_{xy}$ -orbital is responsible for the  $\mathcal{C}$ -band. Within the DFT calculation, the  $d_{xz}$  and  $d_{yz}$  bare bands are relatively flat throughout the entire zone. This is also the characteristic of the observed  $\mathcal{B}$ -band. It is thus natural to assign a dominant  $d_{xz}, d_{yz}$  contribution to this band. The orbital character of the  $\mathcal{A}$ -band is not obviously derived from comparisons to DFT calculations. In principle, photoemission matrix element effects carry information about orbital symmetries. As shown in Fig. 2, the  $\mathcal{A}$ -band displays strong matrix element effects as a function of photon-energy and photon-polarisation. However, probing with 65 eV light, the spectral weight of the  $\mathcal{A}$ -band is not displaying any regularity within the  $(k_x, k_y)$  plane – see supplementary Fig. S1. The contrast between linear horizontal and vertical light therefore vary strongly with momentum. This fact precludes any simple conclusions based on matrix element effects.

**Discussion:** Having explored the orbital character of the electronic states, we discuss the band structure in a more general context. Bare band structure calculations, not including Coulomb interaction, find that states at the Fermi level have  $d_{xy}$  and  $d_{xz}, d_{yz}$  character (see

Fig. 4a). Including a uniform Coulomb interaction  $U$  – acting equally on all orbitals – results in a single Mott gap, inconsistent with the observed flat  $\mathcal{A}$  and  $\mathcal{B}$  bands. Adding in a phenomenological fashion orbital dependent Mott gaps to the self-energy produces two sets of flat bands. However, it is not shifting the bottom of the fast V-shaped dispersion to the observed position. Better agreement with the observed band structure is found, when a Mott gap  $\Delta_{xz,yz} = 1.55$  eV is added to the self-energy of the  $d_{xz}, d_{yz}$  states and a crystal field induced downward shift  $\Delta_{\text{CF}} = 0.6$  eV of the  $d_{xy}$  states is introduced. As shown in Fig. 3c, this reproduces two flat bands and simultaneously positions correctly the fast dispersing  $\mathcal{C}$ -band. From the fact that the bottom of the  $\mathcal{C}$ -band is observed well below the  $\mathcal{B}$ -band, we conclude that an – interaction enhanced – crystal field splitting is shifting the  $d_{xy}$  band below the Fermi level.

A similar structure emerges from DMFT calculations<sup>26</sup> including  $U = 2.3$  eV and Hund's coupling  $J = 0.4$  eV. The obtained spectral function (Fig. 3d) is generally in good agreement with the experimental observations (Fig. 3a). Both the  $\mathcal{C}$  and  $\mathcal{B}$  bands are reproduced with the previously assigned  $d_{xy}$  and  $d_{xz}, d_{yz}$  orbital character (Fig. 4b,c). The  $\mathcal{A}$ -band is also present in the DMFT calculation around  $-0.5$  eV  $< \epsilon < 0$  eV. Even though it is not smoothly connected with the  $\mathcal{C}$ -band, it has in fact  $d_{xy}$  character (Fig. 4b). By analysing the multiplet eigenstates and electronic transitions in the atomic limit of an isolated  $t_{2g}$  shell, we can provide a simple qualitative picture of both observations (Fig. 4d): (i) the energy splitting between the  $\mathcal{A}$  and  $\mathcal{C}$  bands having  $d_{xy}$  orbital character, which we find to be of order  $3J$ , and (ii) the  $d_{xz}$  and  $d_{yz}$  orbital driven  $\mathcal{B}$  band splitting across the Fermi level, found to be of order  $U + J$ . Within this framework, the atomic ground-state has a fully occupied  $d_{xy}$  orbital, while the  $d_{xz}, d_{yz}$  orbitals are occupied by two electrons with parallel



spins ( $S = 1$ ) and thus effectively half-filled. The Mott gap developing in the  $d_{xz}$ ,  $d_{yz}$  doublet is thus  $U + J$  in the atomic limit<sup>5</sup>, corresponding to the electronic transition where one electron is either removed from this doublet, or added to this doublet (leading to a double occupancy). In contrast, there are two possible atomic configuration that can be reached when removing one electron out of the fully filled  $d_{xy}$  orbital (Fig. 4d). One of these final states (high spin) has  $S = 3/2$ ,  $L = 0$  (corresponding pictorially to one electron in each orbital all with parallel spins), while the other (low spin) has  $S = 1/2$ ,  $L = 2$  (corresponding to the case when the remaining electron in the  $d_{xy}$  orbital has a spin opposite to those in  $d_{xz}$ ,  $d_{yz}$ ). The energy difference between these two configurations is  $3J$ , thus accounting for the observed ARPES splitting between the two  $d_{xy}$  removal peaks. Furthermore, this analysis allows to assess, from the experimental value of this splitting  $\sim 1.2$  eV, that the effective Hund's coupling for the  $t_{2g}$  shell is of the order of 0.4 eV. This is consistent with previous theoretical work in ruthenates<sup>27,28</sup> and provides the first direct quantitative estimate of this parameter from spectroscopic experimental data. Because the high spin state is energetically favorable with respect to the low spin state (by  $\sim 3J$ ), it can be assigned to the  $\mathcal{A}$  band near the Fermi level, while the low spin state can be assigned to the  $\mathcal{C}$  band (See Ref. 5 for a detailed description of the atomic multiplets of the  $t_{2g}$  Kanamori Hamiltonian). The Hund's coupling has thus profound impact on the electronic structure of the paramagnetic insulating state of  $\text{Ca}_2\text{RuO}_4$ . The fact that Hund's coupling mainly influence the  $d_{xy}$  electronic states highlights orbital differentiation as a key characteristic of the Mott transition. Moreover, our findings emphasise the importance of the crystal field stabilisation of the  $d_{xy}$  orbital<sup>19,20</sup>. To further understand the interplay between  $U$  and  $J$ , detailed experiments through the metal-insulator transition of  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  would be of great interest.

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**Authors contributions:** R. F., A. V., V. G. grew and prepared the  $\text{Ca}_2\text{RuO}_4$  single crystals. D.S., C.G.F., M. S., F.C., Y.S., G. G., M.G., H.M.R., N.C.P., C.E.M M.S. M.H., T.K.K, J. C., prepared and carried out the ARPES experiment. D.S, C.G.F., F.C, J.C. performed the data analysis. T.R.C, H.-T. J., T.N., made the DFT band structure calculations. M.K and A.G. performed and analysed the DMFT calculations. All authors contributed to the manuscript. D.S. and C.G.F contributed equally.

### Methods

**Experimental:** High-quality single crystals of  $\text{Ca}_2\text{RuO}_4$  were grown by the flux-feeding floating-zone technique<sup>29,30</sup>. ARPES experiments were carried out at the SIS, I05, and MAESTRO beamlines at the Swiss Light Source (SLS), the Diamond Light Source (DLS), and the Advanced Light Source (ALS). Both horizontal and vertical electron analyser geometry were used. Samples were cleaved in-situ using the top-post cleaving method. All spectra were recorded in the paramagnetic insulating phase ( $T = 150$  K), resulting in an overall energy resolution of approximately 50 meV. To avoid charging effects, care was taken to ensure electronic grounding of the sample. Using silver epoxy (EPO-TEK E4110) cured just below  $T = 350$  K (inside the s-Pbca phase – space group 61) for 12 hours, no detectable charging was observed when varying the photon flux.

**DFT+LDA band structure calculations:** We computed electronic structures using the projector augmented wave method<sup>31,32</sup> as implemented in the VASP<sup>33,34</sup> package within the generalized gradient approximation (GGA)<sup>35</sup>. Experimental lattice constants ( $a = 5.39$  Å,  $b = 5.59$  Å and  $c = 11.77$  Å) and a  $12 \times 10 \times 4$  Monkhorst-Pack  $k$ -point mesh was used in the computations with a cutoff energy of 400 eV. The spin-orbit coupling (SOC) effects are included self-consistently. In order to model Mott physics, we constructed a first-principles tight-binding model Hamiltonian, where the Bloch matrix elements were calculated by projecting onto the Wannier orbitals<sup>36,37</sup>, which used the VASP2WANNIER90 interface<sup>38</sup>. We used Ru  $t_{2g}$  orbitals to construct Wannier functions without using the maximizing localization procedure. The resulting 24-band spin-orbit coupled model with Bloch Hamiltonian matrix  $\hat{H}_{\mathbf{k}}^0$  reproduces well the first principle electronic structure near the Fermi energy. To model the spectral function, we added a gap with a leading divergent  $1/\omega$  term to the self-energy  $\hat{\Sigma}(\omega) = \hat{P}_{xz,yz} \Delta_{xz,yz}^2 / \omega + \mathcal{O}(\omega^0)$ . To the Hamiltonian we added a shift  $\hat{H}_{\mathbf{k}} = \hat{H}_{\mathbf{k}}^0 - \hat{P}_{xy} \Delta_{\text{CF}}$ .  $\hat{P}_{xy}$  and  $\hat{P}_{xz,yz}$  are

projectors on the  $d_{xy}$  and  $d_{xz}, d_{yz}$  orbitals respectively, while  $\Delta_{xz,yz}$  is the weight of the poles,  $\Delta_{CF}$  mimics an enhancement crystal field. From the imaginary part of the Green's function  $\hat{G}(\mathbf{k}, \omega) = [\omega - \hat{H}_{\mathbf{k}} - \hat{\Sigma}(\omega)]^{-1}$  with the two adjustable parameters  $\Delta_{CF}$  and  $\Delta_{xz,yz}$ , we obtained the spectral function  $A(\mathbf{k}, \omega)$  by taking the trace over all orbital and spin degrees of freedom.

**DFT+DMFT band structure calculations:** We calculate the electronic structure within DFT+DMFT using the full potential implementation<sup>39</sup> and the TRIQS library<sup>40,41</sup>. In the DFT part of the computation the Wien2k package<sup>42</sup> was used. The LDA is used for the exchange-correlation functional. For projectors on the correlated  $t_{2g}$  orbital in DFT+DMFT, Wannier-like  $t_{2g}$  orbitals are constructed out of Kohn-Sham bands within the energy window  $[-2, 1]$  eV with respect to the Fermi energy. We use the full rotationally invariant Kanamori in-

teraction in order to insure a correct description of atomic multiplets<sup>5</sup>. To solve the DMFT quantum impurity problem, we used the strong-coupling continuous-time Monte Carlo impurity solver<sup>43</sup> as implemented in the TRIQS library<sup>44</sup>. In the  $U$  and  $J$  parameters of the Kanamori interaction, we used  $U = 2.3$  eV and  $J = 0.4$  eV which successfully explains correlated phenomena of other ruthenate such as  $\text{Sr}_2\text{RuO}_4$  and  $\text{ARuO}_3$  ( $A = \text{Ca}, \text{Sr}$ ) within the DFT+DMFT framework<sup>27,28</sup>.

### Competing financial interest:

The authors declare no competing financial interests.

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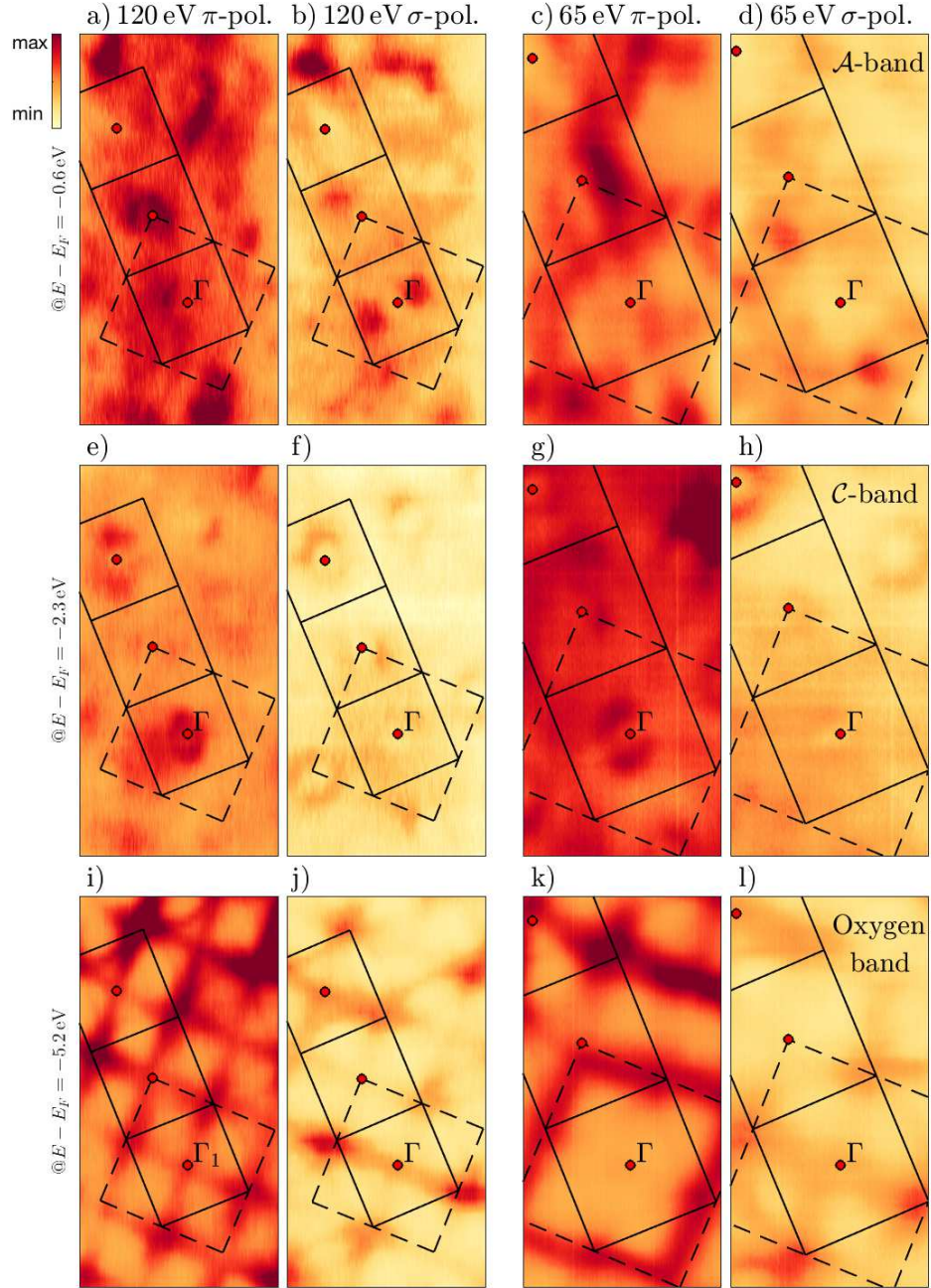
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## I. SUPPLEMENTARY FIGURE: PHOTOEMISSION MATRIX ELEMENTS



Supplementary Figure 1: ARPES intensity maps of ruthenium and oxygen bands in  $\text{Ca}_2\text{RuO}_4$  recorded with 120 eV and 65 eV photons with  $\pi$ - and  $\sigma$ - polarisation. Incident direction of the light is indicated by the blue arrow in (a). These data were recorded with an analyser slit oriented with an angle  $\sim 30$  degrees with respect to the Ru-O bond direction. The orthorhombic zone boundaries are indicated by solid black lines whereas the hypothetical tetragonal zone boundary is displayed with a dashed line. (a)–(d) are constant energy maps at binding energy  $\epsilon = E - E_F = -0.6$  eV revealing the matrix element effects on the  $\mathcal{A}$ -ruthenium band. Notice that the intensities of the  $\mathcal{A}$ -band is strongest for 65 eV (c,d). (e)–(h) are displaying constant energy maps of the  $\mathcal{C}$ -band ( $\epsilon = -2.3$  eV), that is most clearly observed with 120 eV incident photons (e,f). (i)–(l) show intensity maps of the oxygen bands at  $\epsilon = -5.2$  eV.